

Tautomerism of Triarylcarbinols

A Contribution to the Chemistry of Free Radicals

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By

Nathan Edward Van Stone

1916

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This problem was suggested and carried out under the direction of Professor M. Gomberg for whose valuable guidance I wish to express my appreciation.

ANN ARBOR, MICH.,
July 9, 1916.

CONTENTS.

Historical Outline of the Theory of Tautomerism.....	7
Butlerow's Suggestion of Reversible Isomeric Change.....	7
Baeyer's Work on Isatin.....	8
Introduction of the Equilibrium Conception and the Term Tautomerism, by Laar.....	10
Isolation of Two Desmotropes, by W. Wislicenus.....	10
Suggestion of the Term Desmotrope, by Jacobson.....	10
Summary.....	11
 Tautomerism in the Triphenylmethane Series.....	12
The Establishment of the Constitution of the Triphenylmethane Dyes, by E. and O. Fischer.....	12
Application of the Tautomeric Conception to the Constitution of These Dyes by Hantzsch.....	14
Quinocarbonium Theory.....	14
First Isolation of a Pair of Desmotropes in this Series.....	15
Object of this Investigation.....	16
 II. Substituted <i>p</i> -Hydroxytriphenylcarbinols.....	16
General Method for the Preparation of Triarylcarbinols.....	16
 III. Reaction between Benzophenone Chloride and <i>o</i> -Cresol.....	19
Formation of the Diphenoxy Compound.....	20
Preparation of the Desmotropic Forms of the Carbinol.....	21
Dehydration of the Two Forms of the Carbinol.....	22
Preparation of the Fuchsone and Its Acetate.....	23
Preparation of the Tetraphenylated Derivative.....	24
Attempts to Isolate the Free Radical.....	24
Bromination of the Cresylcarbinol and Isolation of Two Desmotropic Forms of the Bromocarbinol.....	25
Chlorination of the Cresylcarbinol and Isolation of Two Desmotropic Forms of the Chlorocarbinol.....	27
 IV. Reaction between Benzophenone Chloride and Guaiacol.....	28
Formation of the Diguaiaoxy Compound.....	29
Isolation of the Two Desmotropic Forms of the Carbinol.....	29
Preparation of the Fuchsone.....	30
Preparation of the Tetraphenylated Derivative.....	30
Bromination of the Guaiacylcarbinol and Isolation of Two Desmotropic Forms of the Brominated Carbinol.....	30
Chlorination of the Guaiacylcarbinol and Isolation of Two Desmotropic Forms of the Chlorinated Carbinol.....	31

V. Reaction between Benzophenone Chloride and <i>o</i> -Bromophenol.....	33
Formation of the <i>o</i> -Bromodiphenoxy Compound.....	33
Preparation of the <i>o</i> -Bromocarbinol by Means of Aluminum Chloride and	
Isolation of the Two Desmotropic Forms of the <i>o</i> -Bromocarbinol	34
Preparation of the Fuchson.....	35
VI. Reaction between Benzophenone Chloride and <i>o</i> -Chlorophenol.....	37
Preparation of <i>o</i> -Chlorophenol.....	37
Formation of the Chlorodiphenoxy Compound.....	38
Preparation of the Chlorocarbinol by Means of Aluminum Chloride and	
Isolation of Two Desmotropic Forms of the Carbinol.....	38
VII. Reaction between Benzophenone Chloride and <i>o</i> -Nitrophenol	40
Preparation of the Nitrocarbinol.....	40
VIII. Summary.....	41

INTRODUCTION.

I. Historical.

It was first clearly recognized by Faraday,¹ in 1825, that two substances might have the same composition and yet possess different properties. Following a previous suggestion of Dalton,² he was able to point out an instance of this nature in the olefines, and drew attention further to the fulminates of Liebig and the cyanurates of Wöhler.

In his *Jahresbericht* for 1829, Berzelius,³ from the study of ammonium cyanate and urea, which had been lately synthesized by Wöhler, concluded that a number of simple atoms may be distributed in a compound in such a way as to give rise to substances with different properties. Two years later when referring to his discovery of racemic acid and its identity in composition to tartaric acid, Berzelius proposed to call such substances *isomeric*.⁴ The number of supposed isomers grew so rapidly and the types of isomerism so differed that the following year Berzelius⁵ introduced the term *polymer* to indicate compounds possessing the same relative proportions but a different number of atoms, and the term *metamer* to denote isomeric compounds so nearly related that they can undergo reciprocal conversion. Unfortunately he chose for his example of metamers cyanic and cyanuric acids, which subsequently were shown to be an example of a reversible polymeric and not a metameric change.

Although the number of polymers and isomers known increased rapidly, there was no case of reversible isomeric change demonstrated until after the development of structural chemistry. In 1877, Butlerow,⁶ from his

¹ *Phil. Trans.*, p. 440 (1825).

² *Mem. Manchester Lit. Phil. Soc.*, [2] 4, 64 (1820).

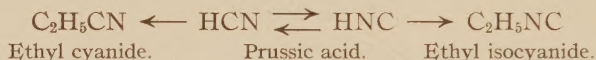
³ *Jahresberichte*, 9, 266 (1829).

⁴ Wöhler's Translation, 44 (1832).

⁵ *Jahresberichte*, 12, 63 (1832).

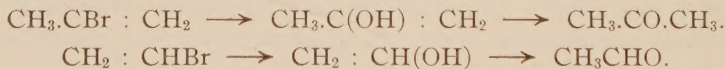
⁶ *Ann.*, 189, 76 (1877).

study of the action of sulfuric acid upon trimethylcarbinol, arrived at the conclusion that a substance of definite chemical constitution may, under the influence of certain catalyzers, suffer a partial change into an isomeric compound and the two remain in equilibrium with each other. Furthermore, he even suggested that such an isomerization might be expected to occur spontaneously in the absence of all catalyzers and an equilibrium between the two isomers might be established. In his own words, "In such cases it is useless to attempt to assign a definite structure to the substance since it consists always of two or more isomeric varieties. It is clear that because of this chemical transformation they react under some conditions as if they contained now one group and now again as another according to the nature of the reagents used and depending upon the conditions of the experiment." As an example of such an isomeric change he pointed to the formation of the isomeric esters from prussic acid.

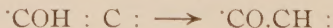


However clear Butlerow's conception of reversible action may have been, it seems to have been forgotten, for we find no mention of it in the earlier discussions of this type of isomerism, although a quarter of a century later after a gradual development, workers in this field arrived again at this same conception of substances in solution changing into isomeric bodies with different structures.

In attempting to prepare propylene alcohol from β -bromopropylene by the usual methods, Linneman found that the product consisted of acetone, similarly vinyl bromide yielded acetaldehyde instead of the isomeric alcohol.¹ By 1880 this behavior appeared so general that Erlenmeyer,² who had made a study of this type of reaction, concluded that "all secondary alcohols in which two bonds of the radical $\overset{\text{|||}}{\text{C}}\text{—OH}$ are saturated by two bonds of a carbon atom are transformed at the moment of their formation into the aldehyde."



This change as may be noted, represents nothing more than the transference of a hydrogen atom from the oxygen to the carbon.



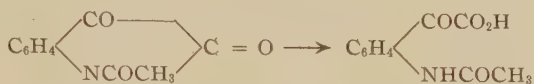
In 1882 Baeyer and Oekonomides,³ in their studies on indigo, observed that isatin is converted into an acetyl derivative by the action of acetic

¹ *Ann.*, **161**, 61 (1872); J. Wislicenus, *Ibid.*, **192**, 119 (1878).

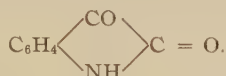
² *Ber.*, **13**, 309 (1881).

³ *Ibid.*, **15**, 2093 (1882); Baeyer, *Ibid.*, **16**, 2188 (1883).

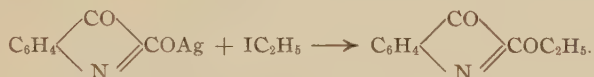
anhydride, and since hydrolysis of this derivative yields acetylisatinic acid, the acetyl group must be linked to the nitrogen



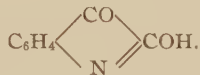
and this would indicate a lactam structure for isatin itself.



On the other hand, isatin forms a silver salt which can be converted into ethyl isatin by the action ethyl iodide and this, on hydrolysis, yields alcohol and isatin.



It follows from this that the ethyl group must have been attached to the oxygen, and the isatin obtainable from the ethyl isatin should possess the lactim structure



However, by hydrolysis in either case Baeyer always obtained the same isatin and not two isomers.

In discussing the structure of isatin and of its ethyl and acetyl derivatives, Baeyer favored the view that there was a single substance, isatin, which under some conditions went into the labile pseudo-form and gave rise to stable derivatives when the imide hydrogen was replaced by groups or radicals. To isatin itself he assigned arbitrarily the lactim structure, and the non-existence of the pseudo-form was accounted for by the wandering of the hydrogen from the nitrogen to the more stable position besides the oxygen.



Closely following this work on isatin came similar examples with Oxindole by Baeyer and Comstock,¹ Hydroxynicotinic acid by von Pechmann,² Methylpseudolutidostyryl by Hantzsch,³ γ -Hydroxyquinaldine by Knorr and Antrik,⁴ and Carbostyryl by Friedlander and Weinberg.⁵ In each of these cases the probable existence of the two modifications of the parent substance was inferred through isolation of stable derivatives obtained

¹ *Ber.*, **16**, 1704 (1883).

² *Ibid.*, **17**, 317, 2387 (1884).

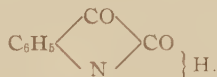
³ *Ibid.*, **17**, 1026, 2903 (1884).

⁴ *Ibid.*, **17**, 2870 (1884).

⁵ *Ibid.*, **18**, 1528 (1885).

from it. These workers used Baeyer's nomenclature and called the labile unisolated isomers the pseudo-forms of their respective compounds.

In 1885, Conrad Laar¹ called attention to the large number of examples of isomerism similar in type to that between isatin and its presumed isomeric pseudo-form. Since these examples differed from the usual conception of isomerism, he proposed the name *tautomerism*. According to Laar there was not one fixed definite structure for isatin but two definite modifications of it existing jointly, *at all times*, and brought about by the constant oscillations of the hydrogen atom between the oxygen and the nitrogen positions.



The credit for the first isolation of two tautomeric forms of a compound is due to W. Wislicenus,² who in 1887 was able to prepare formylphenyl-acetic ester in two modifications, either of which could be easily converted into the other form.



The enol form was a liquid which could be distilled in vacuum without change, whereas the solid keto form when heated to its melting point, was rapidly converted into the enol form.

The result of Wislicenus's work did much to strengthen the views held by Baeyer in opposition to the later views of Laar, but the term *tautomerism*, nevertheless, was retained to signify this specific type of reversible isomeric change. Jacobson³ then suggested that the term *tautomerism* be retained for such cases of assumed isomerism when the two modifications have not been isolated, as in the case of isatin, but for the cases where the separation into the two modifications had been effected, he suggested the term *desmotropism*. In 1896 Knorr,⁴ who with his workers had accomplished much in this field of isomerism, defined uses of both the words *tautomerism* and *desmotropism*, keeping very near to those suggested originally by Jacobson. It is interesting to note that in his definitions of these terms he confined the phenomenon to wanderings of the hydrogen atom only. Such a limitation would evidently exclude from consideration as *tautomerism* similar changes involving shifts of other elements or entire groups, such shifts as were subsequently shown to occur, for example, in the triphenylcarbinol series.

¹ *Ber.*, **18**, 648 (1885).

² *Ibid.*, **20**, 2933 (1887).

³ *Ibid.*, **20**, 1732 (1887).

⁴ *Ann.*, **293**, 70 (1896).

In many instances, as with the original isatin, only one substance is known, the probable existence of the two desmotropic modifications having been inferred from the actual existence of two isomeric series of derivatives. This group is still large and includes, among others, the well-known examples of hydrogen cyanide, methyl pyrazole, cyanuric acid, hydroxy-cafein, and α - and γ -hydroxy-pyridines. In some instances the second or unstable isomer was found capable of existence only while in solution and even then often only temporarily. Such are the pseudo-acids and the pseudo-bases of Hantzsch,¹ the triaryl halides, when in solution in sulfur dioxide,² and probably the free radicals of the type of triphenylmethyl. In each of these cases the presence of the labile form was shown only under specific conditions by either chemical or physical-chemical methods.

Since Wislicenus first isolated the two desmotropic forms of formyl-phenylacetic ester there has been, however, an ever-increasing number of instances of isolation of both modifications. Even acetoacetic ester itself, which for so long a time occupied a most prominent place in the discussion of tautomeric change, was finally resolved into two desmotropic modifications by Knorr,³ who brought about the separation of the two forms by working under most unusual conditions at a very low temperature.

Leaving Butlerow's suggestion out of consideration, the milestones in the historical development of our knowledge of tautomerism may then be said to begin with Baeyer's conception of *one* substance giving rise, under certain conditions, to *two* isomeric sets of derivatives; next, Laar's presumption that the two sets of derivatives indicate the presence, under all conditions, of two forms of the original substance not separable from each other; and finally, the actual isolation of two desmotropic modifications by Wislicenus. Henceforth the conflicting views with regard to tautomerism gradually converged towards the definite conception that tautomerism is merely an instance of spontaneous, reversible, structural isomerization wherein the two individual tautomers require unusually refined methods for their separation only seldom attained.

It is of interest that the conception of enol-ketone-isomerism which is one of the most extensive and important examples of tautomerism, in a measure reverses the deductions of Erlenmeyer, which were previously mentioned, with regard to the shifting of the hydrogen from oxygen to the carbon with the rearrangement of the double bond. It is now necessary to indicate the possibility of the passage of the hydrogen from the carbon to the oxygen with the accompanying rearrangement of the double bond,

¹ *Ber.*, **32**, 575, 3066 (1899).

² Gomberg, *Ibid.*, **42**, 406 (1909).

³ *Ber.*, **44**, 1147 (1911).

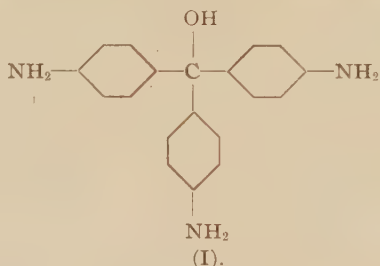
as well as the passage of the hydrogen in the opposite direction, as had been suggested by Erlenmeyer.



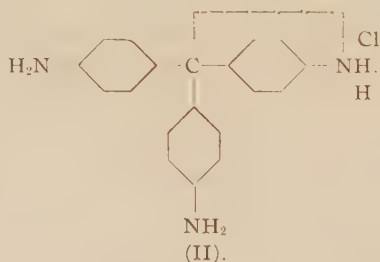
Tautomerization in the Triphenylmethane Series and the Problem of this Investigation.

Although the dyeing properties of basic triphenylmethane derivatives had been discovered as early as 1843 by Hoffmann¹ and had been used for this purpose since the discovery of mauveine by Perkin, the constitution of the substances remained unknown until the researches of E. and O. Fischer,² 1876-1878, through which the constitution of fuchsine and para-fuchsine was determined to be substituted derivatives of triphenylmethane.

The structure of the colorless base of para-rosaniline was shown to be that of an amine, namely, para-triaminotriphenylcarbinol.



The salt which is formed on the addition of an acid to this base is the dye, but its formation from the base does not consist in the mere addition of the acid molecule to the amino group, as is the case with amines in general. The formation of this and similar dyes consists in addition of the acid accompanied by simultaneous loss of a molecule of water, and to this anhydride Fischer assigned the structure



With the acceptance of the Fittig³ structure for quinone in place of the older Graebe⁴ formulation,

¹ *Ann.*, **47**, 73 (1843).

² *Ibid.*, **194**, 242 (1878).

³ Fittig and Siepermann, *Ibid.*, **180**, 23 (1875).

⁴ *Zeit. für Chemie*, **3**, 39 (1867); *Ann.*, **146**, 1 (1868).

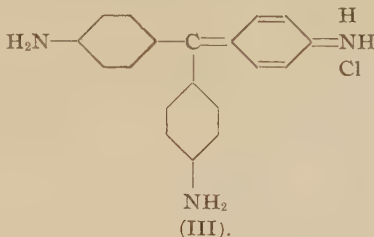


Graebe.



Fittig.

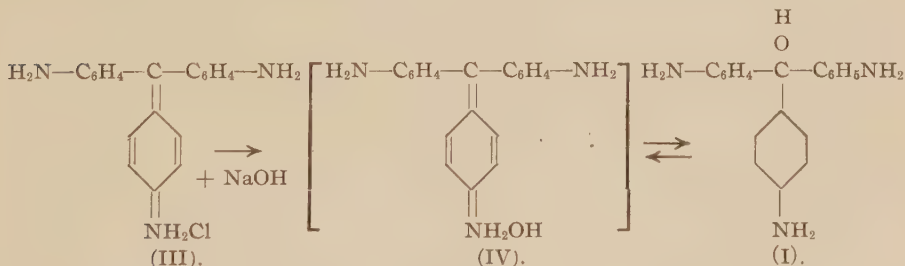
Fischer accepted the Nietzki¹ modification of the original structure of para-rosaniline.



It was thus possible to assign to the colored compounds the ammonium salt structure and at the same time to account of its color attribute by the presence of the chromophor group, the quinoid nucleus, since even the simplest quinones are colored. Similar structures were applied to the many derivatives of the triphenylmethane series, among which were crystal violet, malachite green, fuchsine, etc.

If these ammonium salts are treated with alkali there should be produced the ammonium hydroxide (IV) corresponding to the salt, yet in every instance upon addition of alkali the carbinol (I) is obtained.

With the rise of the tautomeric hypothesis it appeared not impossible to assume that the carbinol obtained and the hypothetical ammonium hydroxide base are tautomeric with each other, the ammonium compound corresponding to the labile form. That one hydroxide, namely the



stable colorless carbinol (I), should exist, is not so strange, provided that two series of isomeric or desmotropic derivatives could be isolated from the parent substance. However, the salts themselves obtained from any of these compounds persisted in occurring in the colored modification alone.

¹ Nietzki, *Farbstoffe Auflage*, I, 88 (1889).

In 1900 the tautomeric interpretation received a fresh impulse through the work of Hantzsch and his co-workers.¹ He was able to show that the salts of crystal violet in solution produce on the addition of alkali a colored water-soluble base, which, like the original salt, is still dissociated to an appreciable extent and which subsequently changes over to the colorless, insoluble, non-dissociated carbinol. He was able to follow this transformation by noting the change in conductivity of the salt before and after addition of an equivalent amount of the alkali. Hantzsch drew the conclusion that the water-soluble transitory compound possessing a marked electrical conductivity must be the true ammonium base. It therefore represents the desmotropic form, while the carbinol subsequently precipitating out from the solution is the stable tautomer. In Hantzsch's nomenclature this evanescent ammonium hydroxide compound is the true base, while the stable carbinol is the *pseudo* base. Henceforth the constitutions of the dyes of the triphenylmethane series were considered as salts of the unstable tautomeric ammonium base, the desmotropic colorless salts of the corresponding stable carbinol modification still remaining unknown.

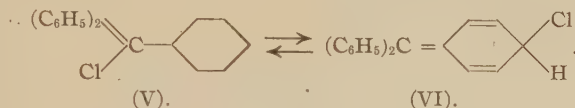
By analogy with these basic dyes the colored derivatives of the triphenylmethane series, devoid of nitrogen but containing oxygen, were also considered as owing their color to the presence of the quinoid nucleus as the chromophor group, although neither in these carbinols nor in their colored derivatives was the isolation of both desmotropic forms accomplished. This applies to such dyes as aurin, benzaurin, phenolphthalein, fluorescein, etc.

The next important step in the application of the tautomeric hypothesis to the triphenylmethane series was taken when it was shown that the hydrocarbon triphenylmethyl, colorless in the solid state, gave rise to colored solutions and that simple non-basic, non-nitrogenous derivatives of this substance were colored. Among the many hypotheses offered was again that of the application of the quinone theory which sought to explain the color of these salt-like derivatives of the carbinol by attributing basic character to carbon atom C^+ (see formula below) and at the same time assuming the presence of the chromophor quinoid nucleus as the cause of the color attribute (VI). These compounds were designated accordingly as quinocarbonium salts.² The quinoid interpretation was not without serious opposition. Here again the carbinols were known only in the one modification, namely the colorless; the acid derivatives were, however, some colorless, as the chloride, others as the

¹ Hantzsch and Kalb, *Ber.*, **32**, 3109 (1899); Hantzsch and Osswald, *Ibid.*, **33**, 278 (1900).

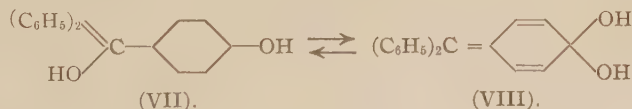
² Kehrmann, *Ibid.*, **34**, 3815 (1901); Gomberg, *Ibid.*, **40**, 1847 (1907); **42**, 406 (1907).

sulfate and double salts, colored. There still lacked for the undoubted basis of the tautomeric conception a single instance of a desmotropic pair of carbinols, one colored and one colorless, or a similar desmotropic pair of derivatives, chlorides, sulfates, or double salts. Evidence of the existence of two forms of such derivatives was at last found in the case of the chlorides.¹ While in solution in ordinary solvents as benzene, chloroform, ether, etc., or when in the solid state, these chlorides are colorless and are correctly assumed to have the constitution of the benzenoid carbinol. When dissolved in liquid sulfur dioxide, however, they give rise to colored solutions and show a totally different chemical behavior from that shown in any other solvent. Their peculiar behavior in this solvent was shown by experimental evidence to be wholly consistent with, and to be explainable only on the assumption that the colored compound possesses the quinonoid constitution (VI).



Thus it was experimentally proven that the color and quinonoid constitution in this class of triphenylmethane derivatives go hand in hand. "There has been supplied in this way a broad experimental basis for this theory."² This proof of the existence of two tautomeric forms of the derivatives of these substances through chemical evidence did much to strengthen the application of the tautomeric hypothesis to the triphenylmethane series, notwithstanding that one of the two desmotropic forms was shown to exist only when in solution and in a particular solvent.

The final long sought for evidence of the two desmotropic forms of the carbinols, colored and colorless, was at last obtained. It has been found that those triphenylcarbinols which have a para substituted hydroxyl group are capable of existence in both the colored and the colorless modifications. Why this should be only with this group and in this particular position is difficult to say, but nonetheless such is the case so far as we know at present. A short, preliminary notice of isolation in the solid crystalline form of two desmotropic modifications of parahydroxytriphenylcarbinol has appeared³ and to these carbinols have been assigned the following structures:

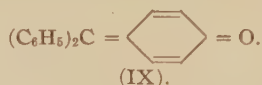


¹ Gomberg, *Ber.*, **40**, 1846 (1907); **42**, 406 (1909).

² Kehrman, *Ibid.*, **40**, 2755 (1907).

³ Gomberg, *THIS JOURNAL*, **35**, 1035 (1913).

Analogy alone should be sufficient to justify the structure assigned to the colored carbinol, analogy with the colored chlorides described in the previous paragraph, and also analogy to the colored fuchsone (IX), the constitution of which could only be



But further, it has been shown that the relative rates of loss of water from each modification on dehydration by means of heat points, beyond doubt, to the close proximity of the two hydroxyl groups in the colored modification. The ease with which the colored modification changes through loss of water into fuchsone is compatible only with the quinonoid structure wherein the two hydroxyl groups are linked to one and the same carbon atom (VIII).

Thus the development of the application of the tautomeric hypothesis to the triphenylmethane derivatives may be summed up as follows: (1) The complex dyes were assumed to be quinonoid, the non-quinonoid desmotropic modification not being known; (2) the dyes on treatment with alkalis gave rise first to unstable colored true bases, which rapidly changed to the carbinols or pseudo-bases; (3) triphenylcarbinol chloride and its analogs were shown to exist in the benzenoid and quinonoid desmotropes, the latter only in solution; (4) a triphenylcarbinol has been isolated in its two desmotropic modifications.

A single carbinol has been reported as existing in two desmotropic forms and it seemed desirable to extend this study to the various substituted triphenylcarbinols, having in view the effects on the tautomeric tendency which might be brought about through substitution of various groups in the benzene ring. Since the greatest effect would probably be brought about through substitution in the same ring with the parahydroxyl group, we have for the present studied the carbinols substituted in this ring and only in those positions ortho to the hydroxyl group. It has been found possible to extend the isolation of the desmotropic forms through a number of substituted carbinols.

II. Substituted *p*-Hydroxytriphenylcarbinols.

Gomberg and Jickling¹ have lately reported a new method for the preparation of *p*-hydroxytriphenylcarbinol by the condensation of benzophenone chloride and phenol. They formulate the reaction as passing through several successive steps in virtue of various intramolecular rearrangements and they have been able to isolate the intermediate products formed.

¹ *J. Am. Chem. Soc.*, **37**, 2575 (1915).

Diphenoxydiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OC}_6\text{H}_5)_2$.

p-Hydroxytriphenylcarbinol, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{OH})$.

Di-*p*-hydroxytetraphenylmethane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$.

We have now studied the condensations of benzophenone chloride with other phenols and have found that this reaction offers a very general method for the synthesis of *p*-hydroxytriphenylcarbinols. We have prepared the carbinols required for our work by this method rather than to use the methods described for this purpose in the literature, which are laborious, involving many steps and giving only meager yields. We have studied the action between benzophenone chloride and the following phenols: *o*-cresol, guaiacol, *o*-bromophenol, *o*-chlorophenol, and *o*-nitrophenol. With the exception of the nitro compound, we have been able to show that a reaction analogous to the first step, as formulated by Gomberg and Jickling, takes place in every case without the aid of a catalytic agent. The various substituted diphenoxydiphenylmethanes have been isolated and are, generally speaking, similar in character and stability to the diphenyl ether of benzophenone. Likewise, the condensation with *o*-cresol, and with guaiacol, proceeded easily through the second step to the formation of the substitutes *p*-hydroxytriphenylcarbinols. With the monobromo- and monochlorophenols it was found that under similar conditions the reaction stopped with the first step, and only the substituted diphenoxydiphenylmethanes could be isolated. It was found that upon addition of the smallest amount of sulfuric acid the reaction between the chloro- or bromophenol and benzophenone chloride proceeded much more vigorously than when the reaction depended upon the hydrochloric acid generated during the course of the condensation. A satisfactory rearrangement of the chloro- and bromophenoxy compounds was only effected when, besides the addition of a drop of sulfuric acid, the reaction mixture was heated for twelve hours at 110° , but this unfortunately brought about decomposition products which made the isolation of the carbinols difficult. Much better results were obtained by substituting aluminum chloride for the sulfuric acid as the condensing agent. In the presence of anhydrous aluminum chloride, using carbon disulfide as a solvent, the reaction between the bromophenol or chlorophenol and benzophenone chloride yielded the desired carbinols, and for our further study this method was employed.

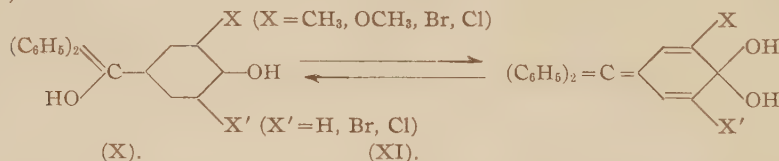
On long standing or when the reaction is carried on at elevated temperatures, benzophenone chloride and phenol yield a tetraphenylated derivative. Under similar conditions we have been able to carry the condensation between the benzophenone chloride and *o*-cresol or guaiacol to analogous compounds.

As previously mentioned, the reaction between *o*-nitrophenol and benzophenone chloride did not proceed in the desired manner. On mixing these

two substances together and slightly warming there was only the slightest evolution of hydrochloric acid gas; with the addition of a drop of sulfuric acid this was only slightly increased. By heating on the water bath there were signs of a more vigorous reaction, but the final product was a charred mass and nothing could be isolated from it. The use of aluminum chloride and carbon disulfide did not yield the desired results. Recourse was finally had by carrying on the reaction between benzophenone chloride and *o*-nitrophenol in the presence of anhydrous aluminum chloride without the use of a solvent, and from this reaction the nitro-substituted carbinol for our work was obtained.

By brominating and by chlorinating the cresyl and guaiacyl carbinols we obtained carbinols substituted in both positions ortho to the para-hydroxyl group, and these also were studied as regards their tendency toward tautomerization. Similarly, the monobromo- and monochloro-carbinols were further brominated and chlorinated, respectively, and the dihalogenated carbinols thus resulting were in their turn investigated.

The Desmotropic Modifications of Substituted *p*-Hydroxytriphenyl-carbinols.—The substitution of various groups in the position ortho to the hydroxyl group did not materially change the general characteristics of the carbinols from those of the *p*-hydroxytriphenylcarbinol itself. In every case save that of the nitro compound we were able to isolate two distinct forms, the colorless benzenoid (X) and the colored quinonoid (XI).



The colorless variety is best obtained by first dissolving the carbinol in normal alkali, precipitating with carbon dioxide and finally crystallizing from such solvents as benzene, ether or alcohol. The second crop of crystals in some cases shows a slight tinge of color, indicating that without doubt the solution contains both forms in equilibrium, but with a predominance of the colorless modification.

The quinonoid modification is always obtained by crystallizing the benzenoid variety from 60 to 70% acetic acid, and in some cases it is necessary to heat the solution for a considerable time to effect a complete change. If recrystallization takes place from more dilute acid, 30 to 40%, the colored modification separates out with less color, higher melting point, and is doubtless a mixture of the two modifications. If stronger acid is used there results in some cases the fuchsone, in others a carbinol acetate. On repeated recrystallization of the quinonoid desmotrope, even without previous treatment with alkali, from benzene,

alcohol, or ether, there is a marked tendency to the formation of the benzenoid variety. The quinonoid carbinols in nearly all instances possess a lower melting point than the corresponding benzenoid modifications.

Although the transformations of the benzenoid modification into the quinonoid take place readily in solution, the identical changes may be brought about to some extent without the use of solvents. With the application of heat the white modification becomes colored, the melting point drops, and eventually, with the loss of a molecule of water, the fuchsone is formed, the rapidity of these various changes being determined by the temperature chosen.

The effect of light energy will also bring about the change from the colorless to the colored modification and, although here the effect, to be sure, is much slower, nevertheless with sufficient time and by occasional stirring in order to expose all of the material to sunlight or light from a mercury lamp, a complete change may be effected.¹

We have assigned, in each case, the benzenoid structure to the white modifications and to the colored carbinols the quinonoid formulation. The benzenoid structure for the colorless carbinols requires no further explanation, it being in harmony with the generally accepted view as regards this class of compounds. Our justification for the quinonoid structure rests upon the analogy to the triaryl halides in the colored form, the relation to the fuchsone, and, particularly, *upon the rate of dehydration under the influence of heat as compared with that of the benzenoid modification*. We have carried out all the dehydrations at a temperature where the transformation from the benzenoid to the quinonoid modification is slow as compared to the loss of water from the colored compound, the temperature in each individual case being also so chosen as to minimize the possible decomposition of the resulting fuchsone. In most cases a temperature of 75° proved the most favorable for our purpose.

III. Reaction between Benzophenone Chloride and *o*-Cresol.

As has been said, the reaction between phenol and benzophenone chloride was found to take place in several successive steps. Between the reaction of phenol and *o*-cresol with benzophenone chloride there is no striking difference. Products which are similar to those isolated with the phenol reaction have been prepared in the course of this work through the reaction of benzophenone chloride upon *o*-cresol. Through the use of a solvent, from which the hydrochloric acid gas generated in the reaction between *o*-cresol and benzophenone chloride may be expelled either by boiling or by the rapid passage of dried air, we have been able to prepare the substituted diphenylether of benzophenone. Without the use

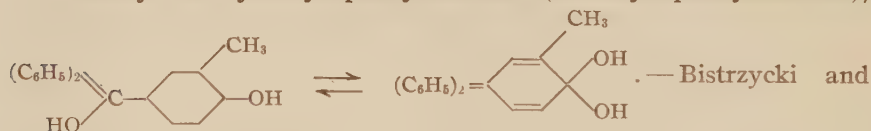
¹ Gomberg, *J. Am. Chem. Soc.*, **35**, 1039 (1913).

of a solvent the condensation proceeds through the second step, yielding 3-methyl-4-hydroxytriphenylcarbinol, and even through the third step, giving 3,3'-methyl-4,4'-hydroxytetraphenylmethane.

2,2'-Methyldiphenoxydiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{C}(\text{OC}_6\text{H}_4\text{CH}_3)_2$.—To the warm solution of 24 g. (1 mol) of benzophenone chloride in 250 cc. of dry benzene are added gradually 27 g. (2.5 mol) of redistilled *o*-cresol. The flask is fitted with a reflux condenser and protected from the moisture of the air by a calcium chloride tube. The solution is gently heated on the water bath, and when no further acid fumes are given off, usually after three to four hours, the reaction may be considered to be at an end. The benzene is evaporated off under reduced pressure and to the yellow oil remaining a few cc. of alcohol are added. Any excess of *o*-cresol or benzophenone chloride that may be present goes into solution in alcohol while the ether separates out as a white solid partly crystalline. For purification it is recrystallized from hot alcohol, and it then melts at 142° . The yield is nearly quantitative. The cresoxy compound is characterized by its insolubility in the ordinary solvents. It is stable to steam distillation, is not soluble nor decomposed by alkalis, but acids decompose it to benzophenone and the *o*-cresol.

Calc. for $\text{C}_{27}\text{H}_{24}\text{O}_2$: C, 85.21; H, 6.36. Found: C, 85.23, H, 6.47.

3 - Methyl - 4 - hydroxytriphenylcarbinol (*o*-Cresyldiphenylcarbinol),



Zurbriggen¹ first prepared *o*-cresyldiphenylcarbinol through the condensation of benzoic acid with *o*-cresol and subsequent removal of the carbon dioxide from the resulting cresyldiphenylacetic acid by use of especially prepared 100% sulfuric acid. The preparation by this method is laborious and the yields are comparatively small. On the other hand, according to our method, an almost theoretical yield of the cresyldiphenylcarbinol is obtained.

24 g. (1 mol) of benzophenone chloride are mixed with 27 g. (2.5 mol) of redistilled *o*-cresol, the mixture is at first cooled, and then allowed to stand at room temperature for from two to four days, protected from the moisture of the air by a calcium chloride tube. After the addition of a little water, the mixture is steam distilled to remove the excess cresol. The residue, after steam distillation, is digested with warm normal alkali and the solution, after cooling, is filtered from benzophenone not carried over in the steam distillation. To remove all traces of benzophenone which may be held in suspension or in solution by the alkali, the solution is shaken with small amounts of ether, and the ether dissolved in the

¹ *Ber.*, **36**, 3558 (1903).

alkaline solution of the carbinol is removed from the solution by passage of a brisk stream of air. To the alkaline solution small amounts of solid sodium chloride are gradually added; on standing the sodium salt of the carbinol crystallizes out in long needles with almost no color. These are filtered, washed with a little water, redissolved in warm water, and the free carbinol is precipitated by passing carbon dioxide into the alkaline solution. On standing, the oily carbinol solidifies and is then filtered and air-dried.

Further purification of the carbinol is best accomplished by converting it into the insoluble acetate (see below) and then regenerating the carbinol. The crude carbinol is dissolved in a small amount of hot glacial acetic acid. On cooling and stirring the entire mass becomes suddenly solid, and the beautiful red crystals of the acetate thus formed may be filtered from the acid, while any tetraphenylmethane derivative that may possibly be present remains in solution in the acid. The red crystals of the carbinol acetate lose their acetic acid when allowed to stand exposed to the air. The resulting fuchsone is now hydrolyzed back to the carbinol by gently warming it with dilute alkalies and some alcohol or acetone, and is then reprecipitated from the solution with carbon dioxide. Further treatment of this carbinol is conditioned upon which of the two desmotropes it is desired to obtain.

The Quinonoid and Benzenoid Desmotropes.—On recrystallization of the purified carbinol from 60% acetic, the quinonoid modification of the carbinol is obtained pure, melting at 108–109° and colored a beautiful yellow. Bistrzycki and Zurbriggen reported that their carbinol melted at 108–109°, was yellow, and on recrystallization the melting point was raised. As a solvent they used acetic acid of 50% strength, and we have also found that with this strength acid the tendency to produce the colorless variety is only hindered by long heating. When the carbinol was precipitated from its alkaline solution by means of dilute acetic acid, Bistrzycki and Herbst¹ obtained a compound identical in composition with the original carbinol yet which, on recrystallization from benzene, was colorless and melted at 148–149°. We have been able to prepare this white variety of the carbinol, namely the benzenoid desmotope, by taking the product precipitated from alkaline solution by carbon dioxide and, after drying, recrystallizing it from alcohol, benzene, or ether and petroleum ether. In every case we were able to obtain a compound identical in composition to the colored carbinol, perfectly white and melting at 148–149°, although often the second batch of crystals showed signs of the colored modification. By dissolving the colorless modification in 60% acetic acid and warming for a short time, the colored carbinol, melting at 108–109°, is obtained. If acid of less strength is used the melting

¹ *Ber.*, 36, 3566 (1903).

point is lowered to 120–130° and the result is a mixture of the two desmotropes possessing a light yellow color. On the other hand, by repeated recrystallization from alcohol or benzene the colored carbinol gradually changes to the white, higher melting, benzenoid desmrotrope. On long exposure in a quartz dish to the rays of the sun, the white modification becomes yellow, but a similar change is noticed in the course of a few hours if the same compound is warmed to 60°.

Calc. for $C_{20}H_{18}O_2$: C, 82.72; H, 6.25. Found: Quinonoid desmrotrope, C, 82.56; H, 6.18; Benzenoid desmrotrope, C, 82.7; H, 6.24.

Dehydration of the Two Forms of the *o*-Cresyldiphenylcarbinol.—Equal amounts of the two desmotropes were heated at the same time in an especially constructed glycerol bath which allowed a very accurate control of the temperature. This bath consisted of a rectangular copper tank measuring $9 \times 6 \times 4$ inches, through the entire length of which extended two copper tubes. When the bath was filled with glycerol and heated, by means of a Bunsen burner beneath, a thermometer which was immersed through an opening in the top into the glycerol showed less than a degree change of temperature during periods extending over several weeks. One gram of each desmrotrope was placed in a porcelain boat about five inches long, the boats placed each in one of the separate tubes, and a slow stream of carefully purified and dried air was passed throughout the period of heating. The rate of dehydration, *i. e.*, the loss of water, was carefully noted at different intervals. While the colored desmrotrope loses water rapidly, the white modification loses it slowly, *in proportion as it is being transformed under the influence of heat energy into the quinonoid desmrotrope*. In the tables below showing the rates of dehydration the time

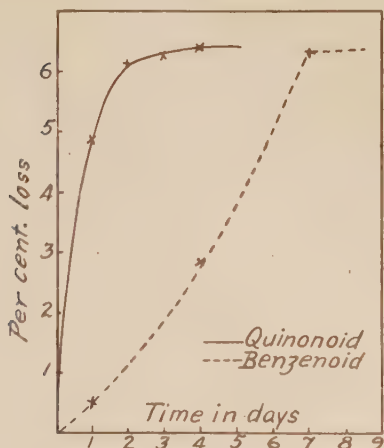


Fig. 1.

represents the different intervals of heating, while the percentages given show the total loss of weight in per cent. at the end of that interval. On longer heating the further loss in either case was on the average of 1 mg. per day, which, as will be shown, is due to the decomposition of the fuchsone itself.

Temperature.	Time.	Quinonoid.	Benzenoid.
70°	24 hrs.	4.86%	0.47%
70°	24 hrs.	6.12%	1.31%
70°	24 hrs.	6.24%	1.81%
70°	24 hrs.	6.38%	2.85%
70°	70 hrs.	6.42%	6.30%

Calculated loss for one molecule of water is 6.25%.

Decomposition of Fuchsones on Heating.—When the dehydration of various carbinols was undertaken at temperatures ranging from 100°

to 150° , it was found that there resulted always a loss considerably more than that calculated for one molecule of water. We have been able to show that at temperatures from 75° and up appreciable decomposition of the fuchsone may take place with the production of small amounts of benzoquinone or its homologs, which are quite volatile, and the loss in weight, on heating the carbinols, in excess of that calculated for one molecule of water is thus accounted for. We have been able to isolate and completely identify benzoquinone resulting in this manner from *p*-hydroxytriphenylcarbinol; tolylquinone, from *o*-cresyldiphenylcarbinol; and methoxyquinone, from 2-methoxy-*p*-hydroxytriphenylcarbinol.

In view of this fact care has to be exercised to select for the dehydration experiments such a temperature that this decomposition would be a minimum, and our results justify the selection of 75° . The facts just described clear up a discrepancy in the observations made by Gomberg, on the one hand, and by Baeyer on the other. Gomberg¹ reported that by the action of silver sulfate on *p*-bromotriphenylchlormethane a *p*-quinone sulfate is produced and that this on hydrolysis yields fuchsone. The latter was not isolated at that time but its presence was inferred from several reasons, among them, by the distinct odor resembling that of benzoquinone. Baeyer² disputed the correctness of this observation claiming that the fuchsone has no odor. The fact that fuchsone on gentle heating does give rise to benzoquinone explains the discrepancy in the two observations. We have now verified that *freshly prepared fuchsone* is without odor, but when kept in a closed bottle, even if only at room temperature, in the course of several days it suffers sufficient autooxidation to give rise to an unmistakable trace of benzoquinone.



When either of the two modifications of the *o*-cresyldiphenylcarbinol are dehydrated, either by heat or by glacial acetic acid, there results the diphenyl-2-methylquinomethane. If the dehydration of the solid forms of the carbinol takes place at a low temperature, this transformation takes place without fusion of the material, and the resulting fuchsone melts at $173\text{--}175^{\circ}$. On recrystallization from benzene, it is obtained as deep red crystals melting at 176° , as described by Bistrzycki and Zurbriggen. It is very soluble in alcohol, ether or acetic acid.

Calc. for $\text{C}_{20}\text{H}_{16}\text{O}$: C, 88.19; H, 5.927. Found: C, 88.02; H, 5.935.

Diphenyl-2-methylquinomethane Acetate.—When either form of the carbinol is dissolved in hot glacial acetic acid and the solution afterwards cooled and stirred the entire mass becomes solid. The deep red crystals

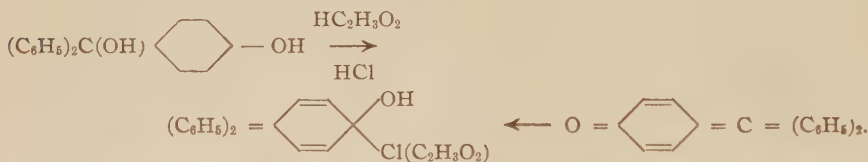
¹ *Ber.*, **40**, 1853 (1907).

² *Ibid.*, **40**, 3086 (1907).

resulting may be filtered off, washed with petroleum ether, dried between filter papers and used for analysis. The same product results if the carbinols are dissolved in the cold and the acid solution is allowed to stand, when the acetate resulting separates out, owing to its lesser solubility. On heating to 75° or on exposure to air the acetate loses the acid, leaving the fuchson. The loss in weight can be checked by passing the acid evolved into a standard alkali solution.

Calc. for $C_{20}H_{16}O + C_2H_4O_2$: $C_2H_4O_2$, 18.08. Found: $C_2H_4O_2$, 18.07, 18.13.

The influence of the *p*-hydroxyl group in inducing tautomerization of this cresyl carbinol to the quinoid state is well brought out by the existence of this colored acetate. Triphenylcarbinol itself also gives an acetate but that one is perfectly white. On the other hand, *p*-hydroxytriphenylcarbinol, when dissolved in sufficient cold glacial acetic acid to make a saturated solution, deposits on standing the acetate intensely colored. Still better results are obtained by starting with the cold saturated solution of the diphenylfuchson. The reaction in this case with acetic acid is not unlike that with hydrochloric acid.



3,3' - Methyl - 4,4' - hydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_3CH_3OH)_2$.—If the reaction mixture between benzophenone chloride and *o*-cresol is allowed to stand several weeks, or if the reaction is carried on at temperatures slightly elevated, the condensation goes to the final step and from the product that results one can isolate appreciable amounts of the substituted tetraphenylmethane.

To 14 g. of benzophenone chloride were added 16 g. of distilled cresol and the mixture was warmed on the water bath for three days. The reaction mixture was then steam distilled to remove the excess of cresol, taken up in normal alkali, the latter shaken with ether to remove the benzophenone, and the product thrown down by the addition of dilute acetic acid to the alkaline solution. On crystallization from dilute acetic acid, it separated out as white crystals melting at 183° , which, on recrystallization from benzene, alcohol, acetic acid or toluene, melt at 190° . Unlike di-*p*-hydroxytetraphenylmethane, this compound is extremely soluble.

Calc. for $C_{29}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 84.82; H, 6.56.

Attempts to Isolate the Free Radical.

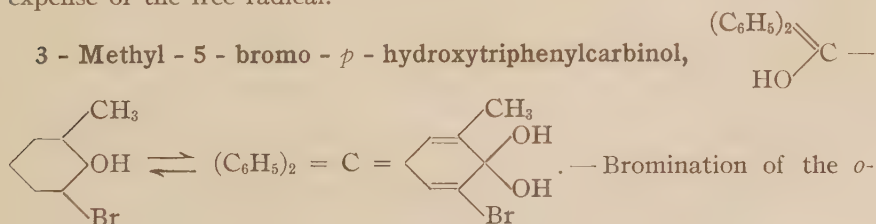
3 - Methyl - *p* - carboethoxytriphenylcarbinol, $C_2H_5O.CO.OC_6H_3CH_3.(C_6H_5)_2COH$.—As the carbinol chloride itself could not be expected to give the free radical the hydroxyl group was protected by the carboethoxy

group. To 30 g. of *o*-cresyldiphenylcarbinol dissolved in as small amount of normal alkali as possible and mixed with ice were added 10 g. (1.1 mol) of chlorocarbonic ester. On standing a granular precipitate separated out which, on recrystallization from acetic acid, melted at 136°.

3-Methyl-*p*-carboethoxytriphenylcarbinol Chloride.—The usual procedure for the preparation of triaryl chlorides was followed, and dry hydrochloric acid gas was passed into a benzene solution of the carbinol. The water formed in the reaction was taken up with a few pieces of fused calcium chloride in the bottom of the flask, and to the benzene solution an equal amount of petroleum ether was added. The chloride separated out in white rosetts. Melting point 131–2°.

Calc. for $C_{23}H_{21}O_3Cl$: Cl, 9.34. Found: Cl, 9.7.

The Free Radical.—The above carbinol and the corresponding chloride were prepared in the hope of obtaining from the latter the free radical which should on gentle hydrolysis yield a hydroxylated triarylmethyl. A preliminary experiment with molecular silver showed that in benzene solution the chloride is readily removed to the extent of 98.5% within ten minutes. When shaken with molecular silver in this way, the solution becomes lemon yellow and, on subsequent exposure to oxygen or air, loses this color and at the same time absorbs oxygen quickly to the extent of 85% of that calculated for one molecule of oxygen, as is usually taken up by the free triarylmethyl radicals. On evaporation of the benzene, a product separates out which bears all the characteristics of a peroxide. The same peroxide is obtained in purer state by shaking the benzene solution of the chloride with silver and simultaneously passing oxygen through the solution, and it then melts at about 161–162°. There can be no doubt therefore that the free radical actually exists, but all our efforts to isolate it in the solid crystalline state proved fruitless. The reason for this failure lies, we believe, in the inherent tendency of this radical to spontaneously polymerize or isomerize when heated, as has been found to be the case with other similar radicals.¹ Indeed, the longer a solution of the radical in ether or benzene is heated the less of the peroxide does it furnish on exposure to air, and at the same time more of a white inactive compound is obtained which is produced at the expense of the free radical.



¹ Gomberg, *Ber.*, 36, 378 (1903); Schlenk, *Ibid.*, 47, 1665 (1914).

cresylidphenylcarbinol takes place in either acetic acid or chloroform. For this purpose the carbinol was dissolved in glacial acetic acid and to this solution was added gradually a large excess of bromine dissolved in the same solvent. After standing at room temperature with occasional shaking, it was warmed on the water bath for a few hours. On cooling slowly there separated out deep red crystals. These were shown, by analysis, to contain bromine substituted in the benzene ring and removable only by drastic treatment, as fusion with sodium peroxide; also bromine which could be easily hydrolyzed off, and in addition bromine that could be titrated by sodium thiosulfate. There can be no doubt that this red compound is a perbromide of a quinonoid-carbinol bromide with apparently three atoms of perbromine, as shown by titration with thiosulfate. Often on cooling too rapidly there separated out along with the crystals of the perbromide a black oil, but this can be put back into solution on application of heat and additional acid.

To obtain the bromocresylcarbinol from this perbromide, two methods may be employed. The red crystals are boiled with a large amount of water; or the perbromide may be taken up in ether, washed with a strong solution of sodium bisulfite in order to remove the bromine, and, after drying the ether solution, the carbinol may be precipitated by addition of petroleum ether. The product resulting in either case is likely to contain a considerable amount of the brominated fuchson. It is, therefore, advisable to redissolve the whole in warm alkali in order to hydrolyze the fuchson, and the carbinol is then precipitated out by addition of dilute acid or by passing carbon dioxide into the solution. On recrystallization from acetic acid 60%, the carbinol is colored red and melts at 138–139°. It represents the quinonoid modification. As was shown to be the case with the *o*-cresylcarbinol, more dilute acid brings about some loss of color in the carbinol and a variable rise in melting point, owing to

the formation of a mixture of the two desmotropes.

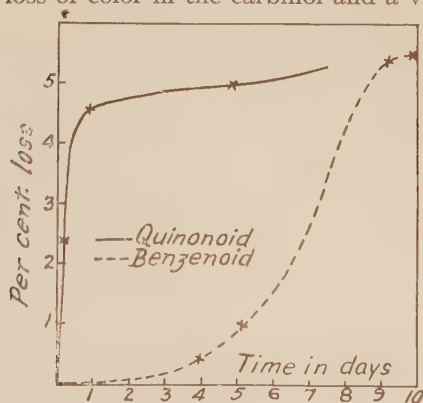


Fig. 2.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOLS.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
75°	3 hrs.	2.4	No loss
75°	22 hrs.	4.54	No loss
75°	24 hrs.	4.75	No loss
75°	24 hrs.	4.90	No loss
90°	48 hrs.	4.97	1.00
105°	120 hrs.	5.40	5.30
105°	48 hrs.	5.40	5.45

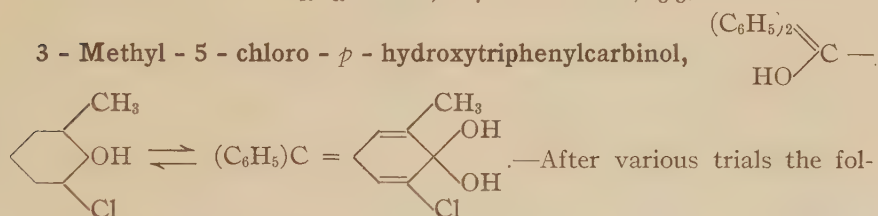
Calculated loss for one molecule of water is 4.89%.

To obtain the colorless desmrotrope, the carbinol is dissolved in normal alkali, precipitated by means of carbon dioxide, and the product obtained filtered, dried, and recrystallized from benzene or ether and petroleum ether. On repeated recrystallization it is obtained entirely white and melts at 145° . The manner of the mutual transformation between these two modifications does not differ greatly from that observed and previously cited in the case of the *o*-cresylcarbinols. On the whole, however, the presence of the bromine in the nucleus imparts to the benzenoid desmrotrope somewhat greater stability in the sense that it shows a lesser tendency to tautomerize to the quinonoid form than the non-brominated carbinol, and may be kept colorless for a longer time than the latter.

Diphenyl-2-methyl-6-bromo-quinomethane, $(C_6H_5)_2C : C_6H_2BrCH_3 : O$.—Dehydration of the carbinol in either desmotropic modification can be carried on at such a temperature that no fusion occurs and yet there results the brominated fuchsone compound. This, on recrystallization from benzene, is orange-red and melts at 202° . It dissolves in the ordinary organic solvents very easily but is insoluble in petroleum ether.

Calc. for $C_{20}H_{16}OBr$: Br, 22.72. Found: Br, 23.3.

3 - Methyl - 5 - chloro - *p* - hydroxytriphenylcarbinol,



lowing procedure was adopted for the chlorination of the *o*-cresylcarbinol: To 16 g. (1 mol) of cresyldiphenylcarbinol suspended in carbon tetrachloride was added chlorine (1 mol) previously dissolved also in carbon tetrachloride. As the reaction proceeds the suspended carbinol goes into solution with evolution of hydrochloric acid gas. Towards the end of the reaction the solution was warmed on the water bath, and then concentrated to a small bulk. On standing there separated out the chlorofuchsone, an orange-colored compound. To hydrolyze it to the carbinol, it was found necessary to warm the fuchsone for a long time with alkali. The carbinol was then precipitated from the alkaline solution by means of carbon dioxide, dried and recrystallized from 60% acetic acid. Unless heated for some time with acetic acid of this strength, quinoidation is likely to be incomplete. The quinonoid desmrotrope thus obtained possesses a yellow color and melts at 133° . If recrystallization of the quinonoid carbinol takes place from alcohol, benzene or ether, the carbinol is partially changed into the colorless desmrotrope. It is, however, difficult to obtain an entirely white compound

in this way except by repeated recrystallizations. If, however, the colored carbinol is first dissolved in normal alkali and then, after reprecipitation with carbon dioxide, is dissolved in any of the above-mentioned solvents, it appears as an entirely white compound, melting at 149° .

The white modification of the chlorocresylcarbinol shows a stability far greater than any of the colorless modifications so far mentioned. This stability shows itself in the dehydration experiment, the white carbinol changing but very slowly into the quinonoid carbinol under the influence of heat; furthermore, even on recrystallization from 60% acetic acid the colorless form persists in crystallizing out unless the solution is previously warmed for some time.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL. TEMP. 75° .

Time of heating.	Quinonoid.	Benzenoid.	Time of heating.	Quinonoid.	Benzenoid.
$1\frac{1}{2}$ hrs.	0.71%	No loss	24 hrs.	5.6%	0.32%
4 hrs.	1.53%	No loss	48 hrs.	5.6%	0.62%
18 hrs.	3.1%	0.12%	72 hrs.	5.7%	1.72%
24 hrs.	4.3%	0.2%	after 12 days	5.7%	5.62%

Theoretical loss due to one molecule of water is 5.54%.

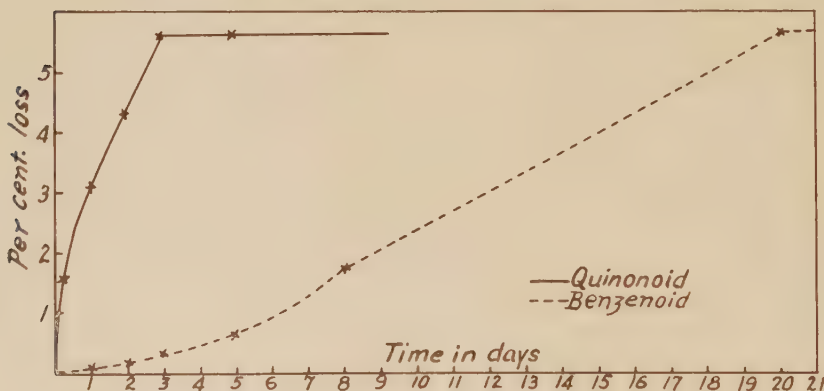


Fig. 3.

Diphenyl-2-methyl-6-chloroquinomethane.—This fuchsone, which results from the dehydration of either modification of the chlorocresylcarbinol, melts at 197° and is far more stable towards heat than most of the other analogs studied. It is easily soluble in most of the usual organic solvents. It is hydrolyzed with difficulty to the carbinol by alkali alone, but if a slight amount of alcohol is added to the alkali solution the carbinol is easily formed and passes into solution.

Calc. for $C_{20}H_{15}OCl$: Cl, 11.58. Found: Cl, 11.42.

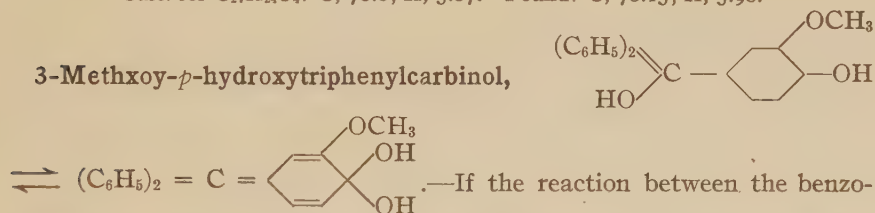
IV. Reaction between Benzophenone Chloride and Guaiacol.

The reaction between benzophenone chloride and guaiacol follows the same course as the condensation of the keto-chloride with either

phenol or *o*-cresol. We have been able to so arrange the conditions as to obtain similar products to those isolated in these previously mentioned cases.

2,2'-Methoxydiphenoxy-diphenylmethane, $(C_6H_5)_2C(OC_6H_4OCH_3)_2$.—To the warmed solution of 24 g. (1 mol) of benzophenone chloride in benzene are added 30 g. (2.5 mol) of distilled guaiacol and the mixture heated on the water bath until the evolution of hydrochloric acid ceases. On evaporation of the excess of benzene a yellow oil separates out which on addition of small amounts of alcohol becomes solid and partly crystalline. This is filtered and recrystallized from hot alcohol or ether, in either of which it is only slightly soluble. When obtained in this manner it is a white compound melting at 189° . Like its analogs already mentioned, it stands steam distillation, is insoluble in alkalis, but acids decompose it into benzophenone and guaiacol.

Calc. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.87. Found: C, 78.15; H, 5.90.



—If the reaction between the benzophenone chloride and guaiacol proceeds in absence of a solvent there results the substituted *p*-hydroxytriphenylcarbinol. This reaction takes place, however, much more slowly than in the case of phenol or *o*-cresol.

In a long-necked round-bottom flask 24 g. (1 mol) of benzophenone chloride are mixed with 30 g. (2.5 mol) of redistilled guaiacol and allowed to stand at room temperature for from two to three weeks. No attempt at cooling is necessary, since the reaction proceeds very slowly and apparently without generation of much heat. The manipulation for isolation of the carbinol differs but little from that employed in the isolation of the *o*-cresol carbinol. After steam distillation to remove the excess of guaiacol the product remains as a yellow oil which solidifies even while warm. This is digested with normal alkali, the solution is cooled and filtered, and the carbinol precipitated by means of carbon dioxide. On standing, this precipitate becomes solid and may be filtered, dried, and recrystallized from benzene. There is probably only the slightest trace of the tetraphenylated derivative present and this remains in solution while the triphenylcarbinol separates out from the hot benzene on slight cooling, being, unlike its analogs, but slightly soluble in this solvent. When obtained in this way the guaiacol compound is entirely white, and melts at 159° . It dissolves in 60% acetic acid with the production of color and after slight warming crystallizes out in the quinonoid modifica-

tion, melting at 147° , and is colored brown. The effects of heat, light, and solvents do not differ in general from those in the case of the carbinols previously mentioned.

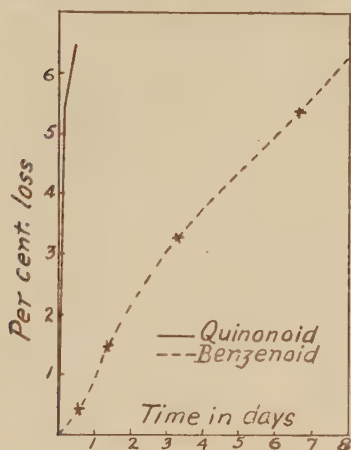


Fig. 4.

Calc. for $C_{20}H_{18}O_2$: C, 78.38%; H, 5.93%. Found (colored desmotrope): 77.92 and 5.72; (white desmotrope): 78.11 and 5.89.

DEHYDRATION OF THE TWO FORMS OF THE CARBINOL.

Temperature.	Time of heating.	Quinonoid.	Benzenoid.
75°	15 min.	0.32%	No loss
75°	15 min.	1.97%	No loss
75°	30 min.	2.94%	0.10%
75°	30 min.	3.94%	0.12%
75°	45 min.	5.39%	0.15%
75°	12 hrs.		0.39%
75°	18 hrs.		1.46%
75°	46 hrs.		3.27%
75°	78 hrs.		5.37%

The loss calculated for 1 mol. of water is 5.24%.

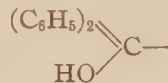
Diphenyl-2-methoxy-quinomethane, $(C_6H_5)_2C : C_6H_3OCH_3 : O$.—The fuchson which results from the dehydration of either form of the guaiacyl carbinol when recrystallized from benzene melts at 183° . It is very soluble in ordinary solvents, is with difficulty hydrolyzed to the carbinol by alkali, but more easily with the addition of slight amounts of alcohol. Of all the fuchsones studied we have found none of them as unstable towards heat as the guaiacyl fuchson. We have been able to isolate the methoxybenzoquinone which results from this decomposition and have found that its melting point is 145° , as reported recently by Moore,¹ and not 140° , as has appeared in the older literature.

2,2'-Methoxydi-*p*-hydroxydiphenylmethane, $(C_6H_5)_2C(C_6H_3OCH_3OH)_2$.—We have been able to obtain this compound in small amounts by carrying on the reaction between benzophenone chloride and guaiacol at elevated temperatures.

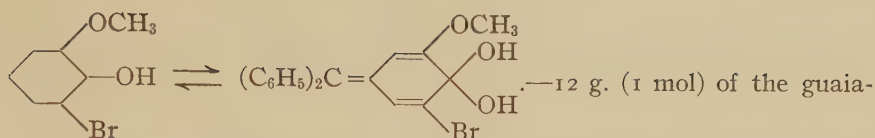
12 g. of benzophenone chloride and 15 g. of guaiacol were mixed and allowed to react for a week at a temperature of 60° to 65° . In working up the reaction mixture in the usual way, there is precipitated from the acetic acid solution on the addition of water small amounts of a high melting compound. It is characterized by its solubility in benzene which renders its separation from the corresponding triphenylcarbinol derivative very simple. On heating it softens at 200° and melts at 208° .

Calc. for $C_{27}H_{24}O_4$: C, 78.6; H, 5.87. Found: C, 78.73; H, 5.56.

3 - Methoxy - 5 - bromo - *p* - hydroxytriphenylcarbinol,



¹ J. Chem. Soc., 99, 1045 (1911).



cyl carbinol were suspended in a small amount of carbon tetrachloride and to this was added bromine (1.1 mol) dissolved in the same solvent. The reaction mixture is warmed on the water bath and finally concentrated to a small bulk. On cooling there separates out the brominated guaiacyl fuchson. The fuchson is hydrolyzed with normal alkali and the free carbinol is obtained in the benzenoid state by precipitation from the alkaline solution by means of carbon dioxide. On recrystallization from ether and petroleum ether it melts at 156° and is entirely white.

The quinonoid modification of the carbinol is obtained when the colorless carbinol is warmed with 60° acetic acid, and on crystallizing from this solvent it is an orange colored substance melting at 151° .

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL.

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
75°	14 hrs.	1.48	0.15	75°	6 days	4.65	2.22
75°	4 days	3.6	0.4	95°	4 days	...	3.52
75°	1 day	3.62	0.57	95°	3 days	...	4.45
75°	3 days	4.1	0.85	95°	2 days	...	4.85

Theoretical loss for one molecule of water is 5.87%.

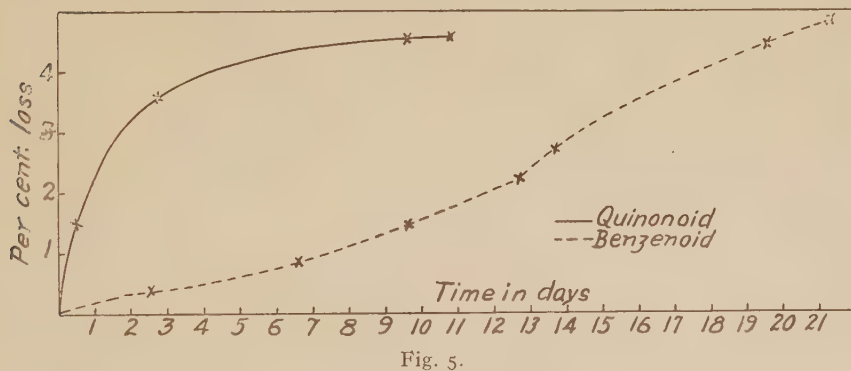
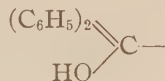


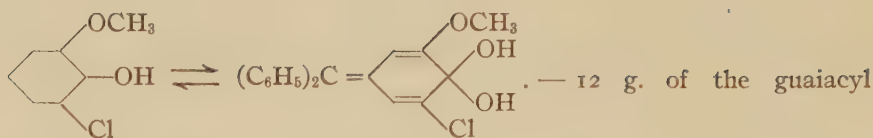
Fig. 5.

Diphenyl-2-methoxy-6-bromoquinomethane. — This bromoguaiacyl-fuchson is obtained by dehydration of either modification of the carbinol. It is stable at 75° , is soluble in benzene and acetic acid, and, when crystallized from either of these solvents, is a dark red compound, melting at 232° .

Calc. for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{Br}$: Br, 21.77. Found: Br, 22.22.

3 - Methoxy - 5 - chloro - *p* - hydroxytriphenylcarbinol,





carbinol were suspended in a small amount of carbon tetrachloride and to this was gradually added the calculated amount (1 mol) of chlorine in solution in carbon tetrachloride. As the reaction proceeds the guaiacyl carbinol goes into solution and there is an evolution of hydrochloric acid gas. Towards the end of the reaction the mixture is warmed on the water bath. The carbon tetrachloride is evaporated and the fuchsonone thus obtained recrystallized from benzene. On long heating, this goes into solution in normal alkali and the chlorinated guaiacyl carbinol is obtained on reprecipitation by means of carbon dioxide. It is then recrystallized from 60% acetic acid, and the quinonoid modification is thus obtained. It is orange colored and melts at 159–161°. It dissolves in alcohol, benzene, or ether, the solution is only slightly colored, and on recrystallization from these solvents there is a marked rise in the melting point of the carbinol accompanied by loss of most of the color. The colorless modification is, however, best obtained by reprecipitation of the carbinol from its alkaline solution with carbon dioxide, and subsequent recrystallization from ether by addition of petroleum ether. When obtained in this manner, it melts at 166–168° and is perfectly white.

DEHYDRATION OF THE TWO MODIFICATIONS OF THE CARBINOL.

Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
75°	9 hrs.	1.5%	0.101%	75°	96 hrs.	5.19%	1.90%
75°	42 hrs.	3.26%	0.496%	95°	220 hrs.	5.35%	4.90%
75°	70 hrs.	4.74%	1.09%	95°	48 hrs.	5.45%	5.21%

Theoretical loss calculated for one molecule of water is 5.26%.

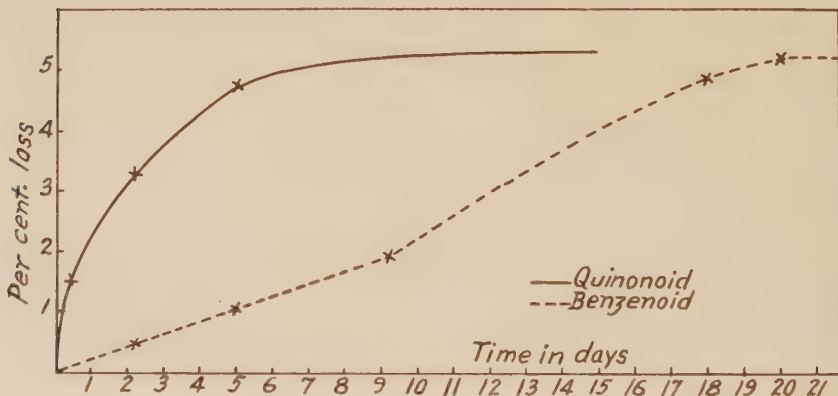


Fig. 6.

Diphenyl-2-methoxy-6-chloroquinomethane.—The chloroguaiacylfuchsonone results from the dehydration of either modification of the carbinol.

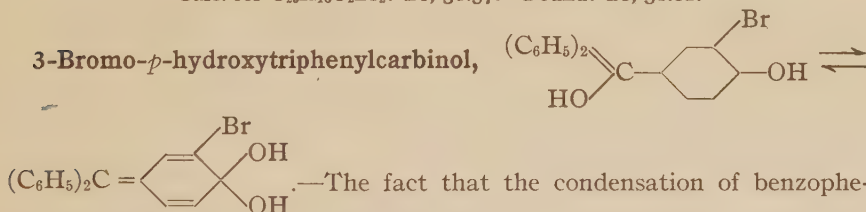
It remains unaffected when heated for a long period at 75° , is soluble in hot benzene, in both these respects differing from the unchlorinated guaiacyl fuchsone. It melts at 227° and on hydrolysis with alkali yields the carbinol.

Calc. for $C_{26}H_{18}O_2Cl$: Cl, 10.98. Found: Cl, 11.01.

V. Reaction between Benzophenone Chloride and *o*-Bromophenol.

2,2'-Bromodiphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_4Br)_2$.—6 g. of benzophenone chloride were mixed with 7 g. of *o*-bromophenol, which had been prepared from *o*-amidophenol by Sandmeyer's reaction. The reaction mixture was allowed to stand at room temperature for several days, no cooling being necessary. During this interval hydrochloric acid was continually given off. The excess of bromophenol was steam distilled, the product digested with normal alkali, but no material soluble in alkali could be isolated, *i. e.*, the condensation under these conditions did not yield any triarylcarbinol. On cooling, the yellow oil solidified and it was found to consist mostly of benzophenone and some of the diphenoxyether, the two being separated from each other by the insolubility of the latter in alcohol. On recrystallization from hot alcohol the ether melts at $184-185^{\circ}$. The theoretical yield of this same product may be obtained by carrying on the reaction between benzophenone chloride and *o*-bromophenol in benzene solution and at a temperature sufficient to expel all the hydrochloric acid formed in the reaction.

Calc. for $C_{26}H_{18}O_2Br_2$: Br, 31.37. Found: Br, 31.82.



none chloride with *o*-bromophenol under the usual conditions, fails to proceed beyond the first step, led us to study more fully the means whereby the phenoxy derivatives may be transformed into the corresponding triphenylcarbinols. A series of experiments on diphenoxydiphenylmethane has shown that this ether gives rise to the carbinol not only under the influence of hydrochloric acid but also when heated in the presence of a very small amount of sulfuric acid. However, when applied to the bromophenoxyether, even this treatment failed to produce more than only a small amount of the carbinol accompanied by a large amount of decomposition products. Nor was the result improved by adding sulfuric acid to the mixture of benzophenone chloride and *o*-bromophenol.¹ We have finally been able to prepare the desired carbinol

¹ Sachs and Thonet, *Ber.*, **37**, 3329 (1904).

by use of these same materials in the presence of anhydrous aluminum chloride in carbon disulfide solution at ordinary temperatures, thus avoiding the decomposition products obtained in the other case.

The procedure used was as follows: 24 g. (1 mol) of benzophenone chloride are dissolved in carbon disulfide and the containing flask surrounded by ice-water. Alternatively there are added small amounts of *o*-bromophenol and finely powdered aluminum chloride until 1.2 mols of each have been added. After the reaction has subsided the mixture is allowed to warm up to room temperature and finally warmed on the water bath. After the evolution of hydrochloric acid gas has ceased the product is cooled and decomposed in the usual manner. The product which separates out as a thick oil is then subjected to steam distillation in order to remove the excess of bromophenol and the product remaining digested with normal alkali. From the filtered solution the sodium salt of the carbinol is precipitated through the addition of solid sodium chloride. The sodium salt is filtered, washed with small amounts of water, redissolved in warm water and the carbinol precipitated by means of carbon dioxide. On standing, the precipitate becomes solid, and is then filtered, dried, and recrystallized from a small amount of carbon tetrachloride. The carbinol resulting is slightly yellow in color, melts at 107–109°, and is entirely white when further recrystallized from ether and petroleum ether. It then melts at 109°.

The colored modification is obtained when acetic acid 60% is used as a solvent. When recrystallized from this solvent, the carbinol is orange in color, and the melting point is 104.5–105°.

That the constitution of this carbinol is that of a *p*-hydroxy compound and not that of the isomeric *p*-bromocarbinol, the production of which is not at all excluded by the process of preparation which has been employed, is proven by the following: On brominating our monobromo compound we get a dibromo compound which is entirely identical with the diphenyl-3-5-dibromo-4-hydroxycarbinol, described by Auwers and Schröten,¹ and the constitution of which can be no other than as given below.

Calc. for $C_{19}H_{16}O_2Br$: Br, 22.51. Found: Br, 23.01.

Dehydration of the Two Modifications of the Carbinol.—Although there is but little variance in the melting points of the two modifications of the bromophenolcarbinols and although the transformation of the white compound to the colored modifications under the influence of heat takes place comparatively easily, yet the difference in rates of dehydration points unmistakably to a difference in structure.

¹ *Ber.*, 36, 3237 (1903).

Temperature 75°.

Time of heating.	Quinonoid.	Benzenoid.
6 hrs.	1.68%	0.43%
19 hrs.	2.95%	1.66%
7 hrs.	3.15%	1.76%
24 hrs.	4.26%	2.13%
13 hrs.	4.71%	2.51%
20 hrs.	5.03%	3.15%
12 hrs.	5.18%	3.43%
7 days	5.21%	5.01%

Calculated loss for one molecule of water is 5.07%.

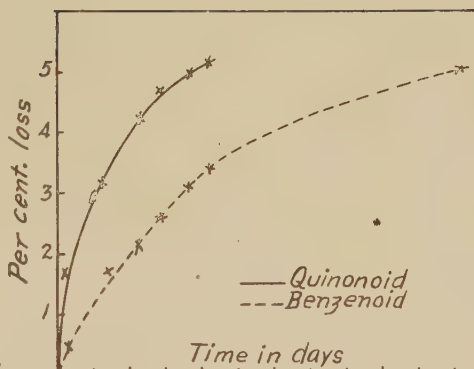
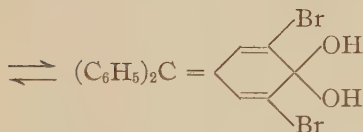
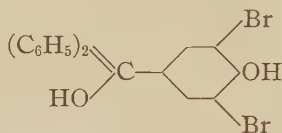


Fig. 7.

Diphenyl - 2 - bromoquinome - thane, $(C_6H_5)_2C : C_6H_3Br : O$. —

The product remaining from the dehydration of either form of the bromocarinol melts at 140° when recrystallized from benzene. This fuchsone is characterized by its low melting point, for all other fuchsones studied melt well over 160°.

3,5 - Dibromo - *p* - hydroxytriphenylcarbinol,



—This carbinol can be prepared, as has been mentioned above, by brominating monobromo-*p*-hydroxytriphenylcarbinol. The more preferable method, however, is to brominate directly *p*-hydroxytriphenylcarbinol. The identity of the dibromides obtained by these two methods proves that the constitution assigned by us to the monobromocarinol as that of *p*-hydroxycarinol is correct.

Both Bistrzycki¹ and Auwers² have worked with the dibromocarinol, have recrystallized it from various solvents, but have failed to notice the existence of it in the two desmotropic forms.

The procedure for the purification of these compounds is as follows: *p*-Hydroxytriphenylcarbinol in acetic acid or in carbon tetrachloride is brominated with the required amount of bromine. The crude solid product is boiled with a small amount of glacial acetic acid. On cooling the insoluble dark orange-red dibromofuchsone crystallizes out, while any unbrominated carbinol remains in solution. The fuchsone is now hydrolyzed to the carbinol by gentle warming with dilute alkali and alcohol,

¹ Bistrzycki and Herbst, *Ber.*, **35**, 3133 (1902).

² Auwers and Schröter, *Ibid.*, **36**, 3237 (1903).

and the carbinol is precipitated by means of a stream of carbon dioxide or with very dilute acetic acid.

In order to obtain the benzenoid desmotrope the carbinol is recrystallized from benzene or from carbon tetrachloride, from which solvents it separated, however, with solvent of crystallization in each case. The crystals from benzene contain one-half molecule of solvent of crystallization, and this is held with considerable tenacity. Samples which have been kept in a desiccator for two weeks still contained about 8% of benzene, while the amount calculated for one-half molecule is 8.24%. The benzene, however, can be driven off at elevated temperatures, about 70°, but the carbinol acquires on this treatment a slight tinge of color. For our dehydration experiments, the carbinol freed from benzene was further recrystallized from ether and petroleum ether.

The preparation of the quinonoid desmotrope requires some care. The carbinol as obtained on the addition of dilute acid to its alkaline solution, is digested while still moist with 80% acetic acid, the filtered solution is gently warmed, and to it hot water is gradually added until the strength of the acid is reduced to about 60%. On cooling the quinonoid modification separates out in red crystals.

Although the two desmotropes differ strictly in their appearance, they both melt at about the same temperature. The purest benzenoid desmotrope melts at 138°, but in most instances the fusion point is found to be 134–136°, and this is the temperature at which the quinonoid modification melts. The colorless carbinol begins to turn quite red at about 90° and it is probable that the benzenoid desmotrope is almost completely converted into the quinonoid desmotrope before the fusion point is reached, and hence the identity of the melting points.

The two desmotropes may be differentiated from each other not only by their difference in color but also by their respective rates of dehydration on heating, as is the case with the pairs of tautomers of the other carbinols described in this paper. In the following experiment we employed, in obtaining the first set of curves, a sample of the benzenoid carbinol which has been obtained from its alkaline solution by treatment with carbon dioxide, washing thoroughly the precipitate and drying in a vacuum desiccator for two weeks. The quinonoid desmotrope employed was the crystalline compound ground to a powder in a mortar. Although the colorless compound was in a much finer state of division, yet the dehydration was slower than that of the colored. It is interesting to note the sudden breaks in the curves with the changes of temperature on heating. In the second experiment both desmotropes employed were crystalline and were reduced to about the same degree of fineness in a mortar and were kept at a constant temperature.

Experiment 1.				Experiment 2.			
Temp.	Time.	Quinonoid.	Benzenoid.	Temp.	Time.	Quinonoid.	Benzenoid.
90°	23 hrs.	1.69	0.47	85°	22 hrs.	0.84	0.18
90°	24 hrs.	2.21	1.01	85°	58 hrs.	2.3	1.06
100-5°	24 hrs.	3.24	2.42	85°	24 hrs.	2.52	1.50
90°	21 hrs.	3.61	3.06	85°	24 hrs.	2.70	1.80
100°	70 hrs.	3.84	3.72	85°	144 hrs.	3.60	3.52
100°	140 hrs.	3.91	3.81				

Calculated loss for one molecule of water was 4.1°.

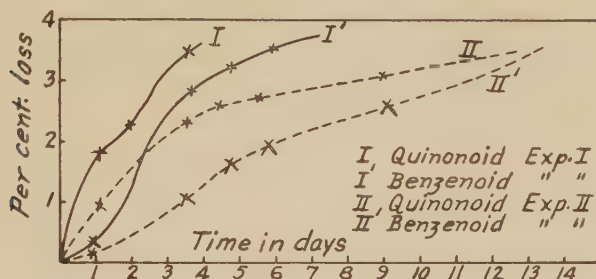


Fig. 8.

VI. Reaction between Benzophenone Chloride and *o*-Chlorophenol.

In the reaction between *o*-chlorophenol and benzophenone chloride the same difficulties and limitations were encountered as in the condensation with bromophenol. The chlorinated phenoxy compound was readily produced, but we were unable to effect its rearrangement except under conditions which rendered the isolation of the triarylcarbinol difficult. Again, as with the bromophenol, we had recourse in the use of anhydrous aluminum chloride.

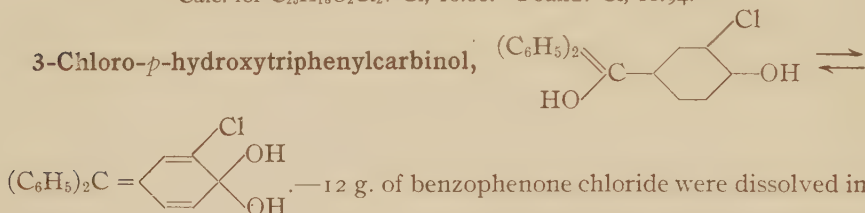
Preparation of *o*-Chlorophenol.—By direct chlorination of phenol there results mostly the *p*-chlorinated compound with relatively small amount of the *o*-chlorophenol. We have tried the various methods reported in the literature, and have found that the method reported by Lossen,¹ chlorinating in carbon tetrachloride solution by means of chlorine dissolved in this same solvent, yielded the best results, 100 g. of phenol yielding as much as 35 g. of the desired compound. For separation from the *p*-chlorophenol, as well as from the unchanged phenol, the method employed by Holleman² was used. The reaction mixture is suspended in potassium carbonate solution and shaken with ether, whereby the unchanged phenol is removed by the ether while the chlorophenols remain in the alkaline solution. This is now acidified, the liberated chlorophenols extracted with ether, the solution dried, and the phenols carefully fractionated.

¹ Friedlander's *Fortschritte*, 7, 89 (1903).

² Holleman and Rinkes, *Rec. trav. chim.*, 30, 79 (1911).

2,2' - Chlorodiphenoxydiphenylmethane, $(C_6H_5)_2C(OC_6H_4Cl)_2$. — The phenoxy compound could be isolated when the reaction between the benzophenone chloride and *o*-chlorophenol was carried out without the use of a solvent, but was more easily prepared, with theoretical yields, if the reaction took place in benzene solution warmed sufficiently to expel the hydrochloric acid gas given off in the reaction as soon as formed. On evaporation of the benzene and the addition of small amounts of alcohol, the chlorophenoxy compound separates out. On recrystallization from hot alcohol, it is obtained quite pure and it then melts at 191–192°.

Calc. for $C_{26}H_{18}O_2Cl_2$: Cl, 16.86. Found: Cl, 16.94.



a small amount of carbon disulfide and the temperature of the solution kept down by means of ice-water. To this solution gradually and alternately small amounts of *o*-chlorophenol and aluminum chloride, finely powdered, were added until slightly more than one molecule of each had been used. The product is isolated in the same manner as the bromophenol compound, and it also is crystallized from carbon tetrachloride, from which it separates as a slightly colored material without a sharp melting point. On recrystallization from 60% acetic acid, the quinonoid desmotope, deep orange and melting at 118°, is obtained. If the product obtained from the carbon tetrachloride solution is dissolved in alcohol, on standing there separates out the benzenoid desmotope in large, transparent, colorless crystals, melting at 70–72°, with apparent loss of solvent of crystallization.

Calc. for $C_{19}H_{15}O_2Cl + \frac{1}{2}C_2H_6O$: $\frac{1}{2}C_2H_6O$, 6.9. Found: $\frac{1}{2}C_2H_6O$, 6.88.

If the alcohol of crystallization is driven off at a low temperature or by long exposure of the crystalline carbinol over calcium chloride, the product remaining is a white powder melting at 126°, and on recrystallization from benzene, or ether and petroleum ether, the melting point is not changed. Similar to the case with the analogous monobromocarbinol, the method employed for the preparation of the 3-chloro-*p*-hydroxytriphenylcarbinol did not exclude the possibilities of production of the isomeric 3-hydroxy-*p*-chlorocarbinol. That the carbinol prepared by the methods just given is nonetheless the *p*-hydroxy compound was definitely shown by further chlorinating the product obtained from this reaction. We obtained in this manner a dichlorocarbinol identical in every respect with the product obtained by direct chlorination of the *p*-hydroxytriphenylcarbinol, the constitution and properties of which are given later in this paper.

The transformation of the 3-chloro-*p*-hydroxytriphenylcarbinol from the white form to the colored modification takes place not quite as readily as with the corresponding bromocarbinol, as can be seen on comparison of the two sets of curves showing the relative values of dehydration.

TEMPERATURE 80°.

Time of heating.	Quinonoid.	Benzenoid.
1 hr.	1.08	
16 hrs.	3.74	2.024
20 hrs.	4.98	2.376
40 hrs.	5.80	3.42
48 hrs.		4.35

Calculated loss for one molecule of water is 5.78%.

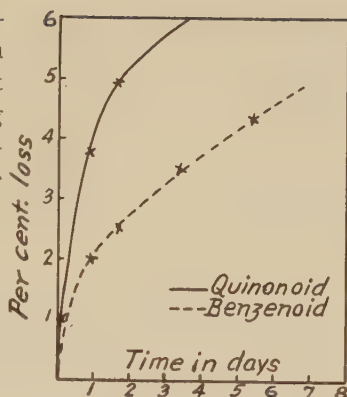
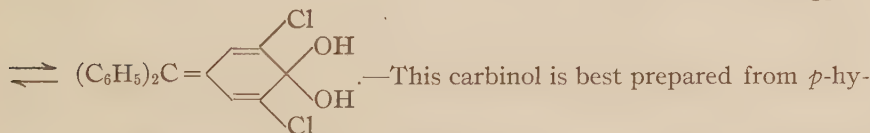
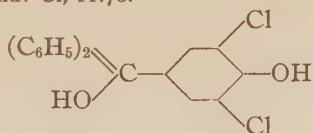


Fig. 9.

Diphenyl-2-chloroquinomethane.—The product remaining from the dehydration of either form of the chlorocarbinol consists of the chlorofuchson. It does not differ in properties from the bromofuchson, both of them showing remarkable stability over the guaiacylfuchson under the influence of heat. When crystallized from benzene it melts at 162–3°. On recrystallization from hot glacial acetic acid there separated out deep red crystals containing acetic acid, which is easily driven off at 75°. Here again, as in the instance of the *o*-cresylfuchson acetate, we are inclined to attribute to this compound the constitution of a quinocarbonium salt, namely, diphenyl-2-chloroquinomethane acetate.

Calc. for $C_{19}H_{14}OCl$: Cl, 11.42. Found: Cl, 11.70.

3,5-Dichloro-*p*-hydroxytriphenylcarbinol,



droxytriphenylcarbinol directly. The latter is suspended in carbon tetrachloride and to the cooled mixture a solution of chlorine in the same solvent is slowly added. The carbinol, on chlorination, goes into solution. The solvent is now evaporated and the residue is boiled up with glacial acetic acid. On cooling, dichlorofuchson, m. p. 217°, very little soluble in cold acetic acid, crystallizes out. The hydrolysis of the fuchson to the carbinol, further purification, and the isolation of the two desmotropes is carried out in the same manner as has been described under the 3,5-dibromocarbinol. The dichlorofuchson is darker red than the corresponding dibromo com-

pound, and the quinonoid carbinol possesses also a brighter red color than the dibromocarbinol. Here again, as has been found to be the case with the analogous dibromocarbinol, the benzenoid dichloro compound crystallizes from benzene and from carbon tetrachloride with solvent of crystallization. Furthermore, the two desmotropes cannot be differentiated from each other by their melting points, for both melt at approximately the same temperature, 134° . They can be differentiated, however, not merely by the difference in color but also by their respective rates of dehydration on heating.

VII. Nitro-*p*-Hydroxytriphenylcarbinol.

The reaction between benzophenone chloride and *o*-nitrophenol was in no way similar to any other condensations previously studied. When mixed in the cold without the use of a solvent there was only slight action as judged from the amount of hydrochloric acid given off. Upon the addition of catalytic agents, a drop of sulfuric and addition of hydrochloric acid gas, this action was only slightly increased. At temperatures ranging from 75 – 100° the evolution of gas was increased, but the resulting product was a charred mass from which nothing could be isolated. Recourse was had to methods similar to those employed with the *o*-bromo- and *o*-chlorophenols, but without satisfactory results, whether carbon disulfide or heptane (b. p. 90°) was used. The condensation was finally brought about in the presence of aluminum chloride without the use of solvents, and resulted in the formation of the nitrohydroxycarbinol. 12 g. (1 mol) of benzophenone chloride and 7.5 g. (1.1 mol) of *o*-nitrophenol are mixed in a round-bottom flask and kept cool by surrounding with ice-water. To this mixture were gradually added 7 g. (1 mol) of anhydrous aluminum chloride. After the reaction is at an end, the mixture is heated on the water bath at 60° . Too high a temperature should be avoided; otherwise the result is a charred mass. After cooling, the aluminum salt is decomposed in the usual manner, the excess of nitrophenol removed by steam distillation, the product digested with normal alkali, precaution being taken to remove the benzophenone, and the sodium salt of the carbinol finally precipitated by addition of sodium chloride. The sodium salts already mentioned of the various carbinols were in every case white needle-like crystals. In the case of the nitrophenolcarbinol the sodium salt was bright red. The carbinol which results from the water solution of the sodium salt on the addition of acids is almost colorless. On recrystallization from 60% acetic acid, it does not change in color but always precipitates out with only a slight amount of color. It melts at 97 – 98° . Recrystallization from any solvent does not change the melting point.

Calc. for $C_{19}H_{17}O_4N$: C, 71; H, 4.71; N, 4.36. Found: C, 70.68; H, 4.353; N, 4.273.

It is barely possible that here we have another instance of substituted triphenylparahydroxycarbinols occurring in but one modification, as is the case in certain carbinols studied in this laboratory by L. C. Johnson and which will be described later. The intense color of the sodium salt, in contradistinction from the carbinol itself, suggests the relation of acinitro to the true nitro compounds, so thoroughly studied by Hantzsch. The substance is now under further investigation.

Summary.

1. It has been shown in this paper that benzophenone chloride condenses with various ortho-substituted phenols, in some instances requiring no catalytic agent, in others the use of aluminum chloride makes the yields more satisfactory. Under proper conditions this offers an excellent method for the preparation of various *p*-hydroxytriphenylcarbinols.

2. It has been shown that substitution of the groups, CH₃, OCH₃, Br, Cl in the ortho positions to the hydroxyl group does not deprive the carbinol of the tendency to tautomerize, and with each carbinol two desmotropic forms have been isolated. The various pairs of tautomers show remarkable similarity, as for example, in their melting points, in every instance the colored compound melting lower than the corresponding white desmotope. Furthermore, the white higher melting compound, through heat or light energy, is invariably changed to the lower melting isomer.

3. Although as mentioned, the substitution did not hinder the tautomeric tendency in the carbinols studied, it resulted nevertheless in a gradation of this tendency. The various curves of dehydration, if placed on one diagram, would show clearly that at the temperature chosen, 75°, the various white desmotropes differ in their readiness to transform into the corresponding colored modifications, as judged by their rate of loss of water. For example, the monobromo-*p*-hydroxytriphenylcarbinol suffers transformation and subsequent dehydration in one-third the time as the chlorocresylcarbinol. Similarly, the colored modifications differ among themselves, as may be noted from the readiness of dehydration of the guaiacyl colored desmotope as compared with the chloroguaiacyl colored compound under similar conditions. This, to be sure, does not indicate tautomeric tendency, but rather serves as a measure of the stability with which the two hydroxyl groups linked to one and the same *p*-quinone-carbon atom are held in the various quinoid carbinols, respectively.

4. The colored desmotropic modifications of the carbinols have been shown to possess the quinonoid constitution. The existence of so large a group of desmotropes removes the phenomenon of tautomerism in this series of compounds from the realm of chance, and offers a very strong support of experimental nature to the whole quinocarbonium theory

and to the quinonoid interpretation of the cause of color in the triphenylmethane series in general. This applies in no lesser degree to the free triarylmethyl radicals themselves. In the solid state they are nearly all colorless or only pale yellow, but when they are dissolved in some solvent, like benzene, intensely colored solutions result. We must assume from the evidence presented in this paper that the radicals dissolve with a simultaneous partial transformation to the quinonoid state.

ANN ARBOR, MICH.

